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TITLE OF THE INVENTION

MULTILAYER COMPOSITE BASED ON POLYAMIDE/POLYOLEFIN

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to a multilayer composite in which a polyamide layer and a polyolefin layer are joined to one another by a bonding agent.

Discussion of the Background

Multilayer composites comprising a polyamide layer and a polyolefin layer are known per se. For example, DE-A 37 15 251 describes a two-layer tube consisting of a polyamide layer and a polyolefin layer for conveying an alcoholic medium. To achieve any adhesion at all between the layers, the polyolefin contains groups derived from maleic acid.

DE-C 40 00 434 describes a multilayer coolant line which, in one embodiment, comprises an outer polyamide layer, an inner polyolefin layer and an intermediate bonding layer of a polyolefin bearing functional groups.

Such composites have firm adhesion between the layers after their production. However, it has been found that adhesion between the layers of functionalized polyolefin and polyamide becomes lower and lower on prolonged contact with aqueous liquids or alcohol-containing fuel, particularly at elevated temperatures, and finally drops to values which are no longer acceptable in practice. The reasons for this are considered to be alcoholysis or hydrolysis reactions.

A different concept is presented in U.S. 3,561,493. There, a mixture of polyamide and polyethylene is recommended as bonding agent between a polyamide layer and a

polyolefin layer. However, attempts to reproduce this disclosure show that, depending on which polymer forms the coherent phase in the mixture, only adhesion either to the polyamide layer or to the polyethylene layer is obtained, but never both at the same time.

Finally, EP-A-1 065 048, which is not a prior publication, describes a multilayer composite comprising a bonding agent which comprises a polyamine-polyamide copolymer. A polyolefin layer or the presence of a polyolefin in the bonding agent is not disclosed there.

SUMMARY OF THE INVENTION

It is an object of the present invention to produce a multilayer composite comprising a polyamide layer and a polyolefin layer joined by a bonding layer which does not consist of a functionalized polyolefin alone.

It is another object to produce a multilayer composite in which the adhesion between layers remains largely intact even on prolonged contact with alcohol-containing media or aqueous media at elevated temperatures.

This and other objects have been achieved by the present invention, the first embodiment of which includes a multilayer composite, comprising:

the following layers bound directly to one another:

a layer I of a polyamide molding composition;

a layer II of a bonding agent comprising at least 50% by weight of a mixture of

a) from 30 to 70 parts by volume of a polymer selected from the group consisting of a polyamide, a polyamine-polyamide copolymer and a combination thereof;

wherein said polyamine-polyamide copolymer is prepared using the following monomers:

α) from 0.1 to 25% by weight, based on the polyamine-polyamide copolymer, of a polyamine containing at least 3 nitrogen atoms, and

β) a polyamide-forming monomer selected from the group consisting of a lactam; a ω-aminocarboxylic acid; an equimolar combination of a diamine and a dicarboxylic acid; and a mixture thereof,

b) from 0.1 to 70 parts by volume of an olefin polymer containing a functional group,

c) from 69.9 to 0 parts by volume of an unfunctionalized polyolefin,

wherein the sum of the parts by volume of a), b) and c) is 100; and

a layer III of a polyolefin molding composition.

Another embodiment of the present invention includes a molding composition, comprising:

at least 50% by weight of the following components:

a) from 30 to 70 parts by volume of a polymer selected from the group consisting of a polyamide, at least 0.1 part by volume of polyamine-polyamide copolymer and a combination of a polyamide and at least 0.1 part by volume of polyamine-polyamide copolymer;

wherein said polyamine-polyamide copolymer is prepared using the following monomers:

α) from 0.1 to 25% by weight, based on the polyamine-polyamide copolymer, of a polyamine containing at least 3 nitrogen atoms, and

β) a polyamide-forming monomer selected from the group consisting of a lactam; a ω-aminocarboxylic acid; an equimolar combination of a diamine and a dicarboxylic acid; and a mixture thereof,

b) from 0.1 to 70 parts by volume of an olefin polymer containing a functional group,

c) from 69.9 to 0 parts by volume of an unfunctionalized polyolefin,

wherein the sum of the parts by volume of, a), b) and c) is 100.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a multilayer composite which comprises the following layers bound directly to one another:

I. a layer I of a polyamide molding composition;

II. a layer II of a bonding agent comprising at least 50% by weight, preferably at least 70% by weight and particularly preferably at least 90% by weight, of a mixture of

a) from 30 to 70 parts by volume of a polymer selected from the group consisting of a polyamide, a branched polyamine-polyamide copolymer and a combination of a polyamide and a branched polyamine-polyamide copolymer;

wherein said branched polyamine-polyamide copolymer is prepared using the following monomers:

α) from 0.1 to 25% by weight, preferably from 0.5 to 20% by weight and particularly preferably from 1 to 16% by weight, based on the polyamine-polyamide copolymer, of a polyamine containing at least 3,

preferably at least 4, particularly preferably at least 8 and very particularly preferably at least 11 nitrogen atoms, and having a number average molecular weight of preferably at least 146 g/mol, particularly preferably at least 500 g/mol and very particularly preferably at least 800 g/mol, and

β) a polyamide-forming monomer selected from the group consisting of a lactam, ω-aminocarboxylic acid and/or an equimolar combination of diamine and dicarboxylic acid,

b) from 0.1 to 70 parts by volume of an olefin polymer containing a functional group,

c) from 69.9 to 0 parts by volume of an unfunctionalized polyolefin,

wherein the sum of the parts by volume of a), b) and c) is 100; and

III. a layer III of a polyolefin molding composition.

The amount of component a) in layer II is preferably 30 to 70 parts by volume, more preferably 40 to 60 parts by volume. The amount of component a) includes all values and subvalues therebetween, especially including 35, 40, 45, 50, 55, 60 and 65 parts by volume.

The amount of component b) in layer II is preferably 0.1 to 70 parts by volume. The amount of component b) includes all values and subvalues therebetween especially including 0.5, 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60 and 65 parts by volume.

The amount of component c) in layer II is preferably 69.9 to 0 parts by volume. The amount of component c) includes all values and subvalues therebetween, especially including 69, 68, 67, 66, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3 and 1 parts by volume.

The amount of the polyamide α) in component a) of layer II is preferably 0.1 to 25% by weight. The amount of polyamine α) includes all values and subvalues therebetween,

especially including 0.5, 1, 2, 3, 5, 10, 15 and 20% by weight.

Preferred polyamides for the layer I or the bonding agent are first and foremost aliphatic homopolycondensates and copolycondensates, for example PA 4B, PA 66, PA 68, PA 612, PA 88, PA 810, PA 1010, PA 1012, PA 1212, PA 6, PA 7, PA 8, PA 9, PA 10, PA 11 and PA 12. The designation of the polyamides corresponds to the international standard, where the first digit(s) indicates the number of carbon atoms in the starting diamine and the last digit(s) indicates the number of carbon atoms of the dicarboxylic acid. If only one number is given, this means that the polyamide has been prepared from an α,ω-aminocarboxylic acid or from the lactam derived therefrom. For further information, reference may be made to H. Domininghaus, Die Kunststoffe and ihre Eigenschaften, pages 272 ff., VDI-Verlag, 1976.

If copolyamides are used, they can comprise, for example, adipic acid, sebacic acid, suberic acid, isophthalic acid, terephthalic acid, naphthalene-2,6-dicarboxylic acid, etc., as coacid and bis(4-aminocyclohexyl)methane, trimethylhexamethylenediamine, hexamethylenediamine or the like as codiamine. Lactams such as caprolactam or laurolactam or aminocarboxylic acids such as ω-aminoundecanoic acid can likewise be incorporated as cocomponents.

The preparation of these polyamides is known (e.g. D.B. Jacobs, J. Zimmermann, Polymerization Processes, pp. 424-467, Interscience Publishers, New York, 1977; DE-B 21 52 194).

Further preferred polyamides are mixed aliphatic/aromatic polycondensates as are described, for example, in U.S. 2,071,250, U.S. 2,071,251, U.S. 2,130,623, U.S. 2,130,943, U.S. 2,241,322, U.S. 2,312,966, U.S. 2,512,606 and U.S. 3,393,210 and also in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd edition, Vol. 18, pages 328 ff. and 435 ff., Wiley

& Sons, 1982. Other preferred polyamides are poly(ether ester amides) or poly(ether amides). Such products are described, for example, in DE-A 25 23 991, DE-A 27 12 987 and DE-A 30 06 961.

The polyamide molding composition can comprise either one of these polyamides or a mixture of a plurality of them. Up to 40% by weight of other thermoplastics can also be present, as long as they do not interfere with the bonding capability. Particularly preferred examples of such further thermoplastics are impact-toughening rubbers such as ethylene-propylene or ethylene-propylene-diene copolymers (EPA-0 295 076), polypentenylene, polyoctenylene, random or block copolymers of alkenylaromatic compounds with aliphatic olefins or dienes

(EP-A-0 261 748) or core/shell rubbers having a tough elastic core of (meth)acrylate, butadiene or styrene-butadiene rubber having a glass transition temperature Tg of $< -10°C$, where the core may be crosslinked and the shell may be made up of styrene and/or methyl methacrylate and/or further unsaturated monomers (DE-As 21 44 528, 37 28 685).

The polyolefin of layer III or of the bonding agent is, for example, polyethylene or polypropylene. It is in principle possible to use any commercial type of polyolefin. Thus, for example, possible polyolefins are: linear polyethylene of high, intermediate or low density, LDPE, isotactic or atactic homopolypropylene, random copolymers of propene with ethane and/or 1-butene, ethylene-propylene block copolymers and the like. The polyolefin can further comprise an impact-toughening component such as EPM or EPDM rubber or SEBS. Furthermore, the customary auxiliaries and additives may also be present. The polyolefin can be prepared by any known process, for example by the Ziegler-Natta process, by the Phillips process, by means of metallocenes or by a free-radical process.

The molding composition of layer III may be crosslinked as described in the prior art

so as to achieve an improvement in the mechanical properties, e.g. the cold impact toughness, the heat distortion resistance or the creep behavior, or in the permeability. Crosslinking is carried out, for example, by radiation crosslinking or by moisture crosslinking of polyolefin molding compositions containing silane groups.

The bonding agent of layer II may further comprise, in addition to the mixture of the components a), b) and c), another polymer or a customary auxiliary and/or additive, as long as these do not significantly impair the bonding action.

Examples of functional groups which may be present in the olefin polymer of component II.b) are acid anhydride groups, N-acyllactam groups, carboxylic acid groups, epoxide groups, oxazoline groups, trialkoxysilane groups and hydroxyl groups. The functional groups can be introduced either by copolymerization of a suitable monomer together with the olefin or by a grafting reaction. In the case of the grafting reaction, a preformed polyolefin is reacted in a known manner with an unsaturated, functional monomer and advantageously a free-radical source at elevated temperature.

The olefin polymers or polyolefins of components b) and c) can be identical or different. For example, it is possible to use an ethylene-propylene rubber functionalized with maleic anhydride groups as component b) and an unfunctionalized isotactic homopolypropylene as component c).

In a preferred embodiment, the bonding agent contains at least 0.1 part by volume of the polyamine-polyamide copolymer and particularly preferably at least 0.5 part by volume. In a further preferred embodiment, the amino group concentration of the polyamine-polyamide copolymer is in the range from 100 to 2500 mmol/kg. The amino group concentration includes all values and subvalues therebetween, especially including 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900,

2000, 2100, 2200, 2300 and 2400 mmol/kg.

As polyamine, it is possible to use, for example, substances from the following classes:

- polyvinylamines (Römpp Chemie Lexikon, 9th edition, Volume 6, page 4921, Georg Thieme Verlag, Stuttgart 1992);
- polyamines which are prepared from alternating polyketones (DE-A 196 54 058);
- dendrimers such as

 $((H_2N-(CH_2)_3)_2N-(CH_2)_3)_2-N(CH_2)_2 \quad N((CR_2)_2 \quad N((CH_2)_3-NH_2)_2)_2$

 (DE-A-196 54 179) or

 tris(2-aminoethyl)amine, N,N-bis(2-aminoethyl)-N',N'-bis[2-[bis(2aminoethyl)amino]ethyl]-1,2-ethanediamine, 3,15-bis(2-aminoethyl)-6,12-bis[2-[bis(2-aminoethyl)amino]ethyl]-9[bis[2-bis(2-aminoethyl)amino]ethyl]amino]ethyl]-3,6,9,12,15-pentaazaheptadecane-1,17-diamine (J.M. Warakomski, Chem, Mat. 1992, 4, 1000-1004);
- linear polyethylenimines which can be prepared by polymerization of 4,5-dihydro-1,3-oxazoles and subsequent hydrolysis (HoubenWeyl, Methoden der Organischen Chemie, Volume E20, pages 1482-'1487, Georg Thieme Verlag, Stuttgart, 1987);
- branched polyethylenimines which are obtainable by polymerization of amidines (Houben-Weyl, Methoden der Organischen Chemie, Volume E20, pages 1482-1487, Georg Thieme Verlag, Stuttgart, 1987) and generally have the following amino group distribution:

 from 25 to 46% of primary amino groups,

from 30.to 45% of secondary amino groups and

from 16 to 40% of tertiary amino groups.

In the preferred case, the polyamine has a number average molecular weight M_n of not more than 20,000 g/mol, particularly preferably not more than 10,000 g/mol and very particularly preferably not more than 5000 g/mol.

Lactams or ω-aminocarboxylic acids used as polyamide-forming monomers contain from 4 to 19, in particular from 6 to 12, carbon atoms. The number of carbon atoms includes all values and subvalues therebetween, especially including 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17 and 18 carbon atoms. Particular preference is given to using ε-caprolactam, ε-aminocaproic acid, caprylolactam, co-aminocaprylic acid, laurolactam, ω-aminododecanoic acid and/or ω-aminoundecanoic acid.

Examples of combinations of diamine and dicarboxylic acid are hexamethylenediamine/adipic acid, hexamethylenediamine/dodecanedioic acid, octamethylenediamine/sebacic acid, decamethylenediamine/sebacic acid, decamethylenediamine/dodecanedioic acid, dodecamethylenediamine/dodecanedioic acid and dodecamethylenediamine/2,6-naphthalenedicarboxylic acid. However, it is also possible to use all other combinations, for example decamethylene diamine/dodecanedioic acid/terephthalic acid, hexamethylenediamineladipic acid/terephthalic acid, hexamethylenediamineladipic acid/caprolactam, decamethylenediamine/dodecanedioic acid/ω-aminoundecanoic acid, decamethylenediamine/dodecanedioic acid/laurolactam, decamethylenediamine/terephthalic acid/laurolactam or dodecamethylenediamine/2,6-naphthalenedicarboxylic acid/laurolactam.

In a preferred embodiment, the polyamine-polyamide copolymer is prepared using, in addition, an oligocarboxylic acid selected from the group consisting of from 0.015 to about 3

mol% of dicarboxylic acid and from 0.01 to about 1.2 mol% of tricarboxylic acid, in each case based on the sum of the other polyamide-forming monomers. In this ratio, diamine and dicarboxylic acid in the equivalent combination of these monomers are each regarded individually. The amount of dicarboxylic acid includes all values and subvalues therebetween, especially including 0.02, 0.05, 0.08, 0.11, 0.14, 0.17, 0.2; 0.25; 0.3; 0.35; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1.0; 1.1; 1,2; 1,3; 1,4; 1,5; 1.6; 1.7; 1.8; 1.9; 2.0; 2.1; 2.2; 2.3; 2.4; 2.5; 2.6; 2.7; 2.8; and 2.9 mol%. The amount of tricarboxylic acid include all values and subvalues therebetween, especially including 0.02; 0.05; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.8; 0.9; 1.0 and 1.1 mol%. If a dicarboxylic acid is used, preference is given to adding from 0.03 to 2.2 mol%, particularly preferably from 0.05 to 1.5 mol%, very particularly preferably from 0.1 to 1 mol% and in particular from 0.15 to 0.65 mol%; if a tricarboxylic acid is used, then preference is given to adding from 0.02 to 0.9 mol%, particularly preferably from 0.025 to 0.6 mol%, very particularly preferably from 0.03 to 0.4 mol% and in particular from 0.04 to 0.25 mol%. The use of the oligocarboxylic acid significantly improves the solvent and fuel resistance, in particular the hydrolysis and alcoholysis resistance.

As oligocarboxylic acid, it is possible to use any dicarboxylic or tricarboxylic acid having from 6 to 24 carbon atoms, for example adipic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, cyclohexane-1,4-dicarboxylic acid, trimesic acid and/or trimellitic acid.

In addition, aliphatic, alicyclic, aromatic, araliphatic and/or alkylaryl-substituted monocarboxylic acids having from 3 to 50 carbon atoms, e.g. lauric acid, unsaturated fatty acids, acrylic acid or benzoic acid, can, if desired, be used as regulators. These regulators enable the concentration of amino groups to be reduced without altering the molecular structure. Furthermore, functional groups such as double or triple bonds, etc., can be

introduced in this way. However, it is desirable for the polyaminepolyamide copolymer to have a substantial proportion of amino groups. The amino group concentration of the copolymer is preferably in the range from 150 to 1500 mmol/kg, particularly preferably in the range from 250 to 1300 mmol/kg and very particularly preferably in the range from 300 to 1100 mmol/kg. The amino group concentration of the copolymer includes all values and subvalues therebetween, especially including 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300 and 1400 mmol/kg. Here and in the following, the term: amino groups refers not only to terminal amino groups but also to any secondary or tertiary amine functions present in the polyamine.

In the polyamine-polyamide copolymer, the composition of the polyamide part can vary within a very wide range since the compatibility with the polyamide of the layer I is obviously determined by other factors and is generally given.

The polyamine-polyamide copolymers can be prepared by various methods.

One possibility is to combine the polyamide-forming monomers and the polyamine and then carry out the polymerization or polycondensation. The oligocarboxylic acid can be added either at the beginning or during the reaction.

However, a preferred method is a two-stage process in which lactam cleavage and the prepolymerization may firstly be carried out in the presence of water (as an alternative, the corresponding ω-aminocarboxylic acids or diamines and dicarboxylic acids are used directly and prepolymerized), after which the polyamine is added in the second step, while any oligocarboxylic acid is introduced before, during or after the prepolymerization. The reaction mixture is then depressurized at temperatures of from 200 to 290°C and polycondensation is carried out in a stream of nitrogen or under reduced pressure. The temperature includes all values and subvalues therebetween, especially including 210, 220, 230, 240, 250, 260, 270

and 280°C.

A further preferred method is hydrolytic degradation of a polyamide to form a prepolymer and simultaneous or subsequent reaction with the polyamine. Preference is given to using polyamides in which the end group difference is approximately zero or in which any oligocarboxylic acid has already been incorporated by polycondensation. However, the oligocarboxylic acid can also be added at the beginning of or during the degradation reaction.

These processes make it possible to prepare ultra highly branched polyamides having acid numbers of less than 40 mmol/kg, preferably less than 20 mmol/kg and particularly preferably less than 10 mmol/kg. A reaction time of from one to five hours at temperatures of from 200°C to 290°C is sufficient to achieve almost complete conversion.

If desired, a reduced pressure phase of a number of hours can follow in a further process step. This has a duration of at least four hours, preferably at least six hours and particularly preferably at least eight hours, at from 200 to 290°C. The temperature includes all values and subvalues therebetween, especially including 210, 220, 230, 240, 250, 260, 270 and 280°C. After an induction period of a number of hours, an increase in the melt viscosity is observed, which may be attributable to a reaction of amino end groups with one another taking place with elimination of ammonia and chain formation. This further increases the molecular weight, which is advantageous for extrusion compositions in particular.

If the reaction is not to be carried out to completion in the melt, the polyamine-polyamide copolymer can also be after-condensed in the solid phase.

The multilayer composite of the invention may further comprise additional layers besides the layers I, II and III, provided that these additional layers adhere to the other layers. Possible additional layers are first and foremost layers having a good barrier action in respect to fuel components, water, alcohols, glycols or gases. These layers consist, in particular, of a

molding composition based on a thermoplastic polyester (e.g. polybutylene terephthalate, polyethylene 2,6-naphthalate, polybutylene 2,6-naphthalate), a fluorinated polymer (e.g. polyvinylidene fluoride, ETFE or THV), an ethylene-vinyl alcohol copolymer (EVOH) or polyoxymethylene.

The molding compositions of layers I, II and III may further comprise up to 50% by weight of additives selected from impact-toughening rubber and/or a customary auxiliary and an additive.

Impact-toughening rubbers for polyamide molding compositions contain functional groups derived from unsaturated functional compounds which are either copolymerized into the main chain or are grafted onto the main chain. Most useful is EPM or EPDM rubber onto which maleic anhydride has been grafted by a free-radical mechanism. Such rubbers can also be used together with an unfunctionalized polyolefin such as isotactic polypropylene, as described in EP-A-0 6883 290.

The molding compositions may also contain relatively small amounts of auxiliaries and additives which are necessary for obtaining particular properties. Preferred examples are plasticizers, pigments or fillers such as carbon black, titanium dioxide, zinc sulfide, silicates or carbonates, processing aids such as waxes, zinc stearate or calcium stearate, flame retardants such as magnesium hydroxide, aluminum, hydroxide or melamine cyanurate, glass fibers, antioxidants, UV stabilizers and additives which give the product antielectrostatic properties or electric conductivity, e.g. carbon fibers, graphite fibrils, fibers of stainless steel or conductive carbon black.

In one possible embodiment, the molding compositions contain from 1 to 25% by weight of plasticizers, particularly preferably from 2 to 20% by weight and very particularly preferably from 3 to 15% by weight. The amount of plasticizers includes all values and

subvalues therebetween, especially including 2, 3, 4, 5, 7, 9, 11, 13, 15, 17, 19, 21 and 23% by weight.

Plasticizers and their use in polyamides are known. A general review of plasticizers suitable for polyamides may be found in Gächter/Muller, Kunststoffadditive, C. Hanser Verlag, 2nd edition, p. 296.

Preferred compounds suitable as plasticizers are, for example, esters of p-hydroxybenzoic acid having from 2 to 20 carbon atoms in the alcohol component or amides of arylsulfonic acids having from 2 to 12 carbon atoms in the amine component, more preferably amides of benzenesulfonic acid.

Particularly preferred plasticizers include ethyl p-hydroxybenzoate, octyl p-hydroxybenzoate, i-hexadecyl p-hydroxybenzoate, N-n-octyltoluenesulfonamide, N-n-butylbenzenesulfonamide or N-2 ethylhexylbenzenesulfonamide.

The multilayer composite of the invention is, in one embodiment, a pipe, a filling port or a container, in particular for conveying or storing liquids or gases, for example in motor vehicles. Such a pipe can be straight or corrugated or have only some corrugated sections. Corrugated pipes are known (e.g. U.S. 5,460,771), so that further details are superfluous. Important applications of such multilayer composites are fuel lines, tank filling ports, vapor lines (i.e. lines in which fuel vapors are conveyed, e.g. breather pipes), filling station pipes, coolant lines, pipes in air conditioning units, lines for clutch fluid, air brake lines, lines for windscreen washers or fuel containers.

The multilayer composite of the invention can also be in the form of a flat composite, for example as a film, such as a packaging film for foodstuffs.

When the multilayer composite of the invention is used for conveying or toning combustible liquids, gases or dusts, e.g. fuel or fuel vapor, it is advisable to make one of the

layers of the composite or an additional interior layer electrically conductive. This can be achieved by compounding with an electrically conductive additive by means of all methods of the prior art. As conductive additive, it is possible to use, for example, conductive carbon black, metal flakes, metal powder, metallized glass spheres, metallized glass fibers, metal fibers (for example of stainless steel), metallized whiskers, carbon fibers (including metallized carbon fibers), intrinsically conductive polymers, e.g. polyaniline, or graphite fibrils. Mixtures of various conductive additives can also be used.

The electrically conductive layer is preferably in direct contact with the medium to be conveyed or stored and has a surface resistance of not none than 10^9 Ω/square, preferably not more than 10^9 Ω/square. The method of determining the resistance of multilayer pipes is described in SAE J 2280 (November 1996, paragraph 7.9).

When the multilayer composite of the invention is configured as a hollow body or hollow profile (e.g. a pipe), this can be additionally sheathed with a further elastomer layer. Suitable sheathing materials include both crosslinking rubber compositions and thermoplastic elastomers. The sheathing can be applied to the pipe either with or without the use of an additional bonding agent, for example by extrusion via a crossflow head or by pushing a prefabricated elastomer hose over the finished, extruded multilayer pipe.

Examples of preferred elastomers are chloroprene rubber, ethylenepropylene rubber (EPM), ethylene-propylene-diene rubber (EPDM), epichlorohydrin rubber (EGO), chlorinated polyethylene, acrylate rubber, chlorosulfonated polyethylene, silicone rubber, plasticized PVC, polyether ester amides or polyether amides.

The multilayer composite can be manufactured in one or more stages, for example by a single-stage process using multicomponent injection molding, coextrusion or coextrusion blow molding, or by multistage processes as described, for example, in U.S. 5,554,425.

To increase the bursting strength, the composite can further comprise a reinforcing textile layer.

The invention also provides the molding compositions of the layer II described here. These can be used not only for the multilayer composite of the invention but also on their own for molded parts of any type.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only, and are not intended to be limiting unless otherwise specified.

Examples

Preparation of a polyamine-polyamide copolymer:

4.78 kg of laurolactam were melted at from 180 to 210°C in a melting vessel and transferred to a pressure-rated polycondensation vessel 250 ml of water and 57 ppm of hypophosphorous acid were then added. The cleavage of the laurolactam was carried out at 280°C under autogenous pressure. The vessel was subsequently depressurized over a period of 3 hours to the vapor pressure of residual water of 3 bar and 230 g of polyethylenimine (LUPASOLO ® 100, BASF AG, Ludwigshafen) were added. The mixture was then depressurized to atmospheric pressure and polycondensation was carried out at 250°C for 2 hours while passing nitrogen over the reaction mixture. The clear melt was discharged as an extruded strand by means of a melt pump, cooled in a water bath and subsequently granulated.

The copolymer obtained had a polyethylenimine content of 4.5% by weight and a PA12 content of 95.5% by weight.

Example 1

45 parts by weight of VESTAMID® ZA7295 (a high-viscosity PA12 for extrusion molding compositions containing an excess of terminal amino groups), 40 parts by weight of NOVOLEN® 2500H (an ethylene-propylene block copolymer from Targor GmbH; extrusion grade), 10 parts by weight of ADMER® Q520E (an isotactic polypropylene grafted with maleic anhydride from Mitsui) and 5 parts by weight of the polyamine-polyamide copolymer prepared above were melted and mixed at 250°C for 5 minutes in a laboratory kneader from Haake.

A 2 mm thick sheet was produced from the resulting compound by pressing at 250°C. In a similar way, 4 mm thick sheets were produced both from VESTAMID® ZA7295 and from NOVOLEN® 2500H by pressing at 240°C.

Subsequently, the following sheets (from the bottom to the top) were placed in the sheet press:

NOVOLEN® 2500H

Compound

VESTAMID® ZA7295.

The upper part of the press had a temperature of 240°C, while the lower part had a temperature of 200°C. The pressing time was 5 minutes.

Adhesion test: Neither the PA12 layer nor the PP layer could be detached from the compound by hand. When a great deal of force was applied, the composite failed instead by rupture of the compound.

Example 2:

45 parts by weight of VESTAMID® ZA7295, 40 parts by weight of NOVOLEN® 2500H, 10 parts by weight of KRATON® FG 1901X (an SEBS grafted with maleic anhydride from Shell) and 5 parts by weight of the polyamine-polyamide copolymer prepared above

were melted and mixed at 250°C for 5 minutes in a laboratory kneader from Haake.

A 2 mm thick sheet was produced from the resulting compound by pressing at 250°C. In a similar way, 4 mm thick sheets were produced both from VESTAMID® ZA7295 and from NOVOLEN® 2500H by pressing at 240°C. The sheets were then pressed together as in Example 1.

Adhesion test: As in Example 1, neither the PA12 layer nor the PP layer could be detached from the compound by hand. When a great deal of force was applied, the composite failed instead by rupture of the compound.

German patent application 10065177.1 filed December 23, 2000, is incorporated herein by reference.

Obviously, numerous modifications and variations on the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.